

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-332261

(43)Date of publication of application : 30.11.2001

(51)Int.Cl.

H01M 4/58

H01M 10/40

(21)Application number : 2000-150317

(71)Applicant : TOYOTA MOTOR CORP

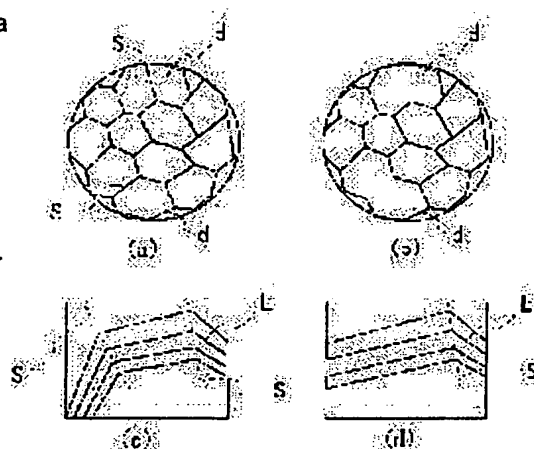
(22)Date of filing : 22.05.2000

(72)Inventor : TAKAGI SHIGEJI

**(54) MANUFACTURING METHOD FOR POSITIVE ELECTRODE ACTIVE SUBSTANCE AND NONAQUEOUS ELECTROLYTIC SOLUTION BATTERY USING POSITIVE ELECTRODE ACTIVE SUBSTANCE****(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide a manufacturing method for a positive electrode active substance of a composite oxide, comprising lithium that can constitute a cell with a less deterioration of a cell capacity and a nonaqueous electrolytic solution cell with the positive electrode active substance.

**SOLUTION:** The manufacturing method for the positive electrode active substance is composed of, at least one of the treatments of a treatment to immerse a composite oxide comprising lithium (nickel acid lithium or the like) with a rock salt structure, in a treating solution composed of more than one kind selected from water, polar organic solvent, and inorganic acid, over 12 hours or more, to yield an average size of a crystal after an immersion for 1.03 time or more than before the immersion, to yield a lattice coefficient of 2.863 to 2.875 Å for an a axis and 14.17 to 14.25 Å for a c axis. The nonaqueous electrolytic solution cell is equipped with the positive electrode comprising the positive electrode active substance manufactured through this method, a negative electrode comprising a material that can absorb and release a lithium ion, and an electrolytic solution comprising a nonaqueous solvent.

**LEGAL STATUS**

[Date of request for examination]

27.11.2002

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

3690242

[Date of registration]

24.06.2005

[Number of appeal against examiner's decision  
of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**CLAIMS**

---

**[Claim(s)]**

[Claim 1] The manufacture approach of the positive active material characterized by performing processing immersed for 12 hours or more into the processing liquid which consists the lithium content multiple oxide which has rock salt structure more than of a kind chosen from water, a polar organic solvent, and an inorganic acid.

[Claim 2] The manufacture approach of the positive active material characterized by performing processing which makes average size of the microcrystal which constitutes this multiple oxide by being immersed into the processing liquid which consists the lithium content multiple oxide which has rock salt structure more than of a kind chosen from water, a polar organic solvent, and an inorganic acid 1.03 or more times before being immersed.

[Claim 3] The manufacture approach of the positive active material characterized by 2.863-2.875Å and a c-axis performing processing to which an a-axis makes the lattice constant of this multiple oxide 14.17-14.25Å by being immersed into the processing liquid which consists the lithium content multiple oxide which has rock salt structure more than of a kind chosen from water, a polar organic solvent, and an inorganic acid.

[Claim 4] The nonaqueous electrolyte cell characterized by having the positive electrode which consists of an active material obtained from claim 1 by the approach of three given in any 1 term, the negative electrode which consists of an ingredient which can carry out occlusion emission of the lithium ion, and the electrolytic solution which consists of a nonaqueous solvent.

---

[Translation done.]

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the nonaqueous electrolyte cell which used the manufacture approach of positive active material, and this positive active material.

[0002]

[Description of the Prior Art] In using a lithium content multiple oxide for the positive active material of a cell, the technique which raises real discharge capacity etc. to JP,10-270025,A by processing this multiple oxide from water or an acid is indicated. Although there is no explanation about the desirable die length of the time amount processed from water or an acid and processing extent for acquiring effectiveness certainly in this official report, in the example, it is immersed in underwater [ containing water or an inorganic acid ] for 0.5 to 2 hours.

[0003]

[Problem(s) to be Solved by the Invention] However, on condition that extent indicated by the example of the above-mentioned official report, the durability of a treatment effect is missing, and the fall of cell capacity cannot fully be controlled in the durability test by the charge-and-discharge cycle. Moreover, in order to acquire desired effectiveness, it was difficult to judge whether processing of a multiple oxide advanced to sufficient extent, without examining by actually assembling a cell.

[0004] The purpose of this invention consists of a lithium content multiple oxide, and even if it repeats charge and discharge, offering the manufacture approach of the positive active material which can constitute few cells has the fall of cell capacity. Using the positive active material manufactured by the above-mentioned approach, even if other purposes of this invention repeat charge and discharge, offering few nonaqueous electrolyte cells has the fall of cell capacity.

[0005]

[Means for Solving the Problem] The manufacture approach of the positive active material the 1st invention in this invention is characterized by performing processing immersed for 12 hours or more into the processing liquid which consists the lithium content multiple oxide which has rock salt structure more than of a kind chosen from water, a polar organic solvent, and an inorganic acid.

[0006] The manufacture approach of the positive active material the 2nd invention is characterized by performing processing which makes average size of the microcrystal which constitutes this multiple oxide 1.03 or more times before being immersed by being immersed into the processing liquid which consists the lithium content multiple oxide which has rock salt structure more than of a kind chosen from water, a polar organic solvent, and an inorganic acid.

[0007] The manufacture approach of the positive active material the 3rd invention is characterized by 2.863-2.875Å and a c-axis performing processing to which an a-axis makes the lattice constant of this multiple oxide 14.17-14.25Å by being immersed into the processing liquid which consists the lithium content multiple oxide which has rock salt structure more than of a kind chosen from water, a polar organic solvent, and an inorganic acid.

[0008] And the nonaqueous electrolyte cell of the 4th invention is characterized by having the positive electrode which consists of an active material obtained by the approach of the 1st

invention – the 3rd invention, the negative electrode which consists of an ingredient which can carry out occlusion emission of the lithium ion, and the electrolytic solution which consists of a nonaqueous solvent. Hereafter, this invention is explained to a detail.

[0009] (1) The compound which will not be limited especially if it has rock salt structure and may function as positive active material as a “lithium multiple oxide” used for this invention about a lithium content multiple oxide, for example, is expressed with a chemical formula  $\text{LiMO}_2$  can be used. The “rock salt structure” which the above-mentioned multiple oxide has is expressed with the crystal structure shown in drawing 1. As M in a chemical formula  $\text{LiMO}_2$ , a kind or two sorts or more of metals chosen from Co, nickel, Mn, aluminum, Fe, Cr, and Zn may be desirable, in addition may be a cobalt atom in a cobalt acid lithium, and a metal of replaceable arbitration. Among these, especially the compound that are a kind or two sorts or more of metals with which M is mainly chosen from Co, nickel, and Mn is desirable, and the nickel acid lithium whose 60% or more (preferably 70% or more) of M is nickel is the most desirable. Although especially the manufacture approach of this nickel acid lithium is not limited, after using nickel  $(\text{NO}_3)_2$  and nickel  $(\text{OH})_2$ ,  $\text{NiCO}_3$ ,  $\text{NiO}$ ,  $\text{NiOOH}$ , etc. as a source of nickel, using  $\text{LiOH}$ ,  $\text{LiNO}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Li}_2\text{O}_2$ , etc. as a source of a lithium and mixing both, the manufacture approach of performing about 600 degrees C – 900 degrees C heat treatment is common among an oxygen air current.

[0010] (2) The “processing liquid” immersed in the above-mentioned multiple oxide about processing liquid consists more than of a kind chosen from water, a polar organic solvent, and an inorganic acid. What has a polarity comparatively near water as the above “a polar organic solvent”, and does not have a bad influence on the activity of a lithium multiple oxide is desirable. For example, six or less (3 or less [ Preferably ]) carbon atomic number alcohol, a ketone, an organic acid, etc. are used preferably, and can mention methyl alcohol, ethyl alcohol, an acetone, formic acid, an acetic acid, etc. as an example. Moreover, it is desirable to be able to use a hydrochloric acid, a nitric acid, a sulfuric acid, etc., among these to use the hydrochloric acid from a point or nitric acid of a cycle property as the above “an inorganic acid.”

[0011] As processing liquid used for this invention, it is desirable to use the mixed solvent of water, a polar organic solvent, or a water and a polar organic solvent. Although especially the mixing ratio of the water and the polar organic solvent in a mixed solvent is not limited, water/polar solvent can set it to 95 / 5 – 5/95 (preferably 85 / 15 – 15/85, still more preferably 70 / 30 – 30/70) by the weight ratio, for example. When using an inorganic acid, it is desirable to use in the amount from which the concentration in processing liquid is set to 0.001N–0.1N (preferably 0.005N–0.05N).

[0012] (3) Perform processing immersed in this processing liquid in the above-mentioned lithium content multiple oxide in the manufacture approach of the positive active material of this invention about processing conditions. In the 1st invention, it may be “12 hours or more (preferably 16 hours or more, more preferably 20 hours or more)” by making extent of the processing into immersion time amount. Since cell capacity tends to deteriorate in the durability test by the charge-and-discharge cycle in the nonaqueous electrolyte cell by which the durability of a treatment effect was insufficient for immersion time amount, and it was constituted in less than 12 hours using this positive active material, it is not practical. Although especially the upper limit of immersion time amount is not limited, since a treatment effect is mostly saturated with processing of 24 hours or more, it is desirable to consider as 100 or less hours from the point of manufacture effectiveness. As for the above-mentioned multiple oxide, it is desirable to be immersed in processing liquid as powder of particle size (for example, mean particle diameter of 0.01–500 micrometers, preferably 0.1–100 micrometers, still more preferably 1–30 micrometers) which was suitable as an active material. At this time, it is usually 0–60 degrees C, as for the temperature of processing liquid, it is desirable to consider as 10–50 degrees C, and it is still more desirable to consider as 20–40 degrees C.

[0013] Moreover, immersion processing is performed to extent “makes 1.03 or more (preferably 1.06 or more times, more preferably 1.09 or more times) times before immersion” average size of the microcrystal which constitutes a lithium content multiple oxide in the 2nd invention. The endurance of processing of change of average size in less than 1.03 times is inadequate. Although especially the upper limit of change of average size is not limited, they are usually 10 or

less times. "Microcrystal" means each single crystal field d which constitutes a lithium content multiple oxide here, as shown in drawing 2 (a) and (c). Usually, although the array of Grid L serves as mismatching in the interface S of adjoining microcrystal, the rearrangement of Grid L happens with immersion processing, and the grids L of adjoining microcrystal turn into one microcrystal together by some interfaces S at this time [ drawing 2 (b) and (d)]. This phenomenon is observed as a rise of the average size of microcrystal. In addition, it can ask for the average size of microcrystal from an X diffraction result. For example, what is necessary is to calculate an integral value using the Cauchy (Cauchy) function in the case of a nickel acid lithium, and just to compute to it from the peak in an X diffraction Fig. (1 1 3). In addition, in the nickel acid lithium compounded by the usual liquid phase process, the average size of microcrystal is about 55nm.

[0014] Moreover, in the 3rd invention, immersion processing is performed to extent which presupposes "2.863-2.875Å (preferably 2.865-2.875Å) and a c-axis are 14.17-14.25Å (preferably 14.18-14.25Å) for an a-axis" the lattice constant of a lithium content multiple oxide. The crystal orientation indicated to be the a-axis and c-axis in a lithium content multiple oxide to drawing 1 here is pointed out. Increase of this lattice constant is imagined to be what is produced when a part of Li in a multiple oxide is eluted in processing liquid. In addition, it can ask for a lattice constant from the usual X diffraction result etc. An a-axis is [ 2.861Å and the c-axis of the lattice constant of the nickel acid lithium compounded by the usual liquid phase process ] about 14.17Å.

[0015] (4) The positive electrode in the nonaqueous electrolyte cell of this invention is equipped with the positive active material obtained by the manufacture approach of the 1st - the 3rd invention about a nonaqueous electrolyte cell. For example, it comes to form a positive-active-material layer on the charge collector which consists of metallic foils, such as aluminium foil, a nickel foil, and copper foil, etc. by applying the positive-active-material paste containing this positive active material and solvents, such as N-methyl pyrrolidone, and drying. The thickness of the above-mentioned charge collector is usually about 5-100 micrometers. The configuration of a charge collector can be made into the shape of band-like or a rectangle etc. according to the configuration of a cell, and can also make the magnitude the thing of arbitration according to capacity etc.

[0016] As for the above-mentioned positive-active-material layer, it is desirable in addition to positive active material, to usually contain a binder and to contain electric conduction-ized material further. Polyvinylidene fluoride (PVDF) etc. is used as the above-mentioned binder, and carbon materials, such as carbon black, a graphite, and pitch coke, are preferably used as electric conduction-ized material. It is desirable that the rate of each component in a positive-active-material layer makes this whole active material layer 100 % of the weight, and make positive active material into extent 70 to 99% of the weight (preferably 80 - 98 % of the weight), and it makes extent and electric conduction-ized material extent for a binder 0.5 to 25% of the weight (preferably 1 - 15 % of the weight) 0.5 to 25% of the weight (preferably 1 - 15 % of the weight).

[0017] Moreover, the negative electrode in this cell consists of "ingredients (negative-electrode active material) which can carry out occlusion emission of the lithium ion", such as carbon materials, such as amorphous carbon and graphite, or a metal lithium. For example, it comes to form a negative-electrode active material layer by applying the negative-electrode active material paste which contains this negative-electrode active material and solvents, such as N-methyl pyrrolidone, in the charge collector which consists of the same ingredient as a positive electrode, and drying. As for this negative-electrode active material layer, it is desirable to carry out extent content of the binders, such as PVDF, for a negative-electrode active material 0.5 to 25% of the weight (preferably 1 - 15 % of the weight) 75 to 99.5% of the weight (preferably 85 - 99 % of the weight), using this whole active material layer as 100 % of the weight.

[0018] A kind chosen from the various aprotic solvents used for the conventional rechargeable lithium-ion battery as a "nonaqueous solvent" as the electrolytic solution or two sorts or more can be used. For example, ethylene carbonate (EC), propylene carbonate (PC), gamma-butyrolactone, 1, 2-dimethyl ethane, a tetrahydrofuran, 1, 3-dioxane, methyl acetate, diethyl

carbonate (DEC), etc. are mentioned. Moreover, as an electrolyte, the various lithium salt,  $\text{LiPF}_6$  and  $\text{LiBF}_4$ , used for the conventional rechargeable lithium-ion battery,  $\text{CF}_3\text{SO}_3\text{Li}$ , and  $\text{LiClO}_4$  grade can be used, and  $\text{LiPF}_6$  and  $\text{LiBF}_4$  are [ among these ] desirable. [ for example, ] The electrolytic concentration in the electrolytic solution is usually 0.05 – 10 mol/L extent, and is 0.1 – 5 mol/L extent preferably.

[0019] (An operation and effectiveness) Although the reason whose endurance of cell capacity improves by the above-mentioned immersion processing is not necessarily clear, the following devices can be considered, for example. That is, by immersing the above-mentioned lithium content multiple oxide in the above-mentioned processing liquid, a part of Li in this multiple oxide is eluted in processing liquid, it permutes by the proton, and a lattice constant increases. At this time, the rearrangement of a crystal lattice happens and the size of microcrystal becomes large (crystallinity improves). The crystal structure at the time of the charge condition from which Li was desorbed serves as stability by this, generation of the site which cannot return Li is controlled, and it is imagined as that by which the fall of positive-electrode capacity is suppressed as the result. It is desirable that elution extent of Li sets the number of Li(s) after 1 and immersion to  $(1-A)$ , and sets the number of Li(s) in the chemical formula showing the presentation of the lithium content multiple oxide before immersion to  $0.01 < A \leq 0.5$ , and it is  $0.02 < A \leq 0.2$  more preferably. When A is too large, since the amount of Li in connection with charge and discharge will decrease, it is not desirable. The value of this A can be calculated by the ICP AEM method.

[0020] According to the positive active material obtained by the manufacture approach of this invention, the cell capacity after 1000 charge-and-discharge cycle trials can obtain the nonaqueous electrolyte cell excellent in endurance of 55% or more (desirable conditions 60% or more), being able to use cell capacity immediately after test initiation as 100%.

[0021]

[Embodiment of the Invention] Hereafter, an example and the example of a comparison explain this invention still more concretely.

(1) Water was put into the manufacture beaker of positive active material, after the powder (mean particle diameter of 6 micrometers) of the nickel acid lithium (presentation;  $\text{Li}_1\text{nickel}_{0.8}\text{Co}_{0.15}\text{aluminum}_{0.05}\text{O}_2$ ) obtained by the liquid phase process was immersed at the room temperature for 0.5 to 72 hours, the vacuum drying of 24 hours was performed at 120 degrees C, and the positive active material of examples 1-4 and the examples 2-3 of a comparison was obtained.

[0022] It is attached to the nickel acid lithium (example 1 of a comparison) which does not perform each positive active material and immersion processing which were obtained. (1 0 4) of an X diffraction Fig., (0 1 5), (1 1 3), A-axis length and c-axis length are computed by performing elaboration of a lattice constant using the peak of (0 0 12), (0 2 4), and (0 1 11). The integral value was calculated using the Cauchy (Cauchy) function from the peak, and moreover (1 1 3) computed the magnitude of microcrystal. The X diffraction Fig. and attribution of each peak are shown in drawing 3 about the nickel acid lithium manufactured in the example 1. In addition, the analysis conditions of an X diffraction are as follows.

[The analysis conditions of an X diffraction]

X-ray; -- CuK alpha-rays voltage-of-X-ray-tube; -- 50kVX line tube electric current; -- 300mA of values of A which shows Li elution rate was calculated by the ICP AEM method again by setting the presentation of the nickel acid lithium after immersion to  $\text{Li}(1-A)$   $\text{nickel}_{0.8}\text{Co}_{0.15}\text{aluminum}_{0.05}\text{O}_2$ . The above result is shown in Table 1.

[0023]

[Table 1]

表 1

	比較例			実施例			
	1	2	3	1	2	3	4
処理時間 (hr)	0	0.5	2	12	24	48	72
Li 溶出割合(Aの値)	0	<0.01	<0.01	0.028	0.055	0.10	0.14
a 軸長 (Å)	2.861	2.861	2.861	2.863	2.865	2.868	2.870
c 軸長 (Å)	14.17	14.17	14.17	14.17	14.18	14.19	14.20
結晶子の平均サイズ(nm)	55	55	55	57	60	60	60

[0024] (2) The nickel acid lithium of the example 1 acquired by the manufacture above of a nonaqueous electrolyte cell, an example 2, and the example 1 of a comparison was used for positive active material, respectively, and the nonaqueous electrolyte cell was produced. The positive electrode equipped with the positive-active-material layer which consists of the following weight ratios was obtained by applying the positive-active-material paste containing the graphite as the nickel acid lithium as positive active material, and electric conduction-ized material, and PVDF as a binder to the above-mentioned charge collector, and drying, using aluminium foil as a charge collector for positive electrodes. N-methyl pyrrolidone was used as a solvent of a paste.

[A presentation of a positive-active-material layer]

Nickel acid lithium / graphite / PVDF=90/5/5[0025] Moreover, the negative electrode equipped with the negative-electrode active material layer which consists of the following weight ratios was obtained by applying the negative-electrode active material paste containing PVDF as the graphite and the binder as a negative-electrode active material to the above-mentioned charge collector, and drying, using copper foil as a charge collector for negative electrodes. N-methyl pyrrolidone was used as a solvent of a paste.

[A presentation of a negative-electrode active material layer]

Graphite / PVDF=95/5[0026] The cylindrical cell of the structure shown in drawing 4 was constituted using the positive electrode and negative electrode which were produced above. Namely, on both sides of the separator 13 which consists of polyethylene, sheet-like a positive electrode 11 and a negative electrode 12 were piled up in between, and it stored in the closed-end cylinder-like sheathing can 14 by making this into the shape of a roll. This sheathing can 14 functions also as a negative-electrode terminal. Moreover, the electrolytic solution (not shown) sinks into the separator 13. Then, the positive-electrode terminal 15 was put on the opening edge of the sheathing can 14, it fixed with the seal packing 16, and the nonaqueous electrolyte cell 1 of cell capacity 1000mAh was obtained. In addition, as the electrolytic solution, the mixed solvent (the weight ratio of EC/DEC = 3:7) of EC and DEC containing LiPF<sub>6</sub> of 1 mol/L was used.

[0027] (3) the charge-and-discharge cycle trial was performed on the following conditions to the performance-evaluation profit \*\*\*\* nonaqueous electrolyte cell, and the endurance of cell capacity was evaluated. The result is shown in drawing 5. In drawing 5, cell capacity (capacity maintenance factor) when an axis of ordinate makes the time of durability test initiation 100%, and an axis of abscissa are the numbers of charge-and-discharge cycles. In addition, for the example 1, 1060mAh(s) and an example 2 were [1080mAh(s) and the examples 1 of a comparison of the cell capacity at the time of durability test initiation] 1040mAh(s).

[Charge-and-discharge cycle test condition]

Temperature; the cycle of 60-degree-C charge-and-discharge cycle; "2C charge (up to 4.1V) → pause 10 minute → 2C discharge (up to 3.0V) → pause 10 minute" is repeated.

[0028] Moreover, the relation between the cell capacity after 1000 cycle termination (capacity maintenance factor when making the time of test initiation into 100%) and the magnitude of the microcrystal of a nickel acid lithium, and the immersion time amount to the processing liquid at the time of positive-active-material manufacture is shown in drawing 6.

[0029] By immersion processing of 0 - 2 hours, as shown in Table 1, although change is not seen



by the crystal structure, a lattice constant and the average size of microcrystal increase by immersion processing of 12 hours or more, and clear increase is seen by processing of 24 hours or more. And the cell capacity maintenance factor after a durability test is improved by immersion processing of 12 hours, in processing of 24 hours or more, distinct improvement is found and this result is mostly in agreement with the stage when increase of the average size of microcrystal or a lattice constant starts so that drawing 5 and drawing 6 may show.

[0030]

[Effect of the Invention] According to the manufacture approach of this invention, in performing predetermined immersion processing to a lithium content multiple oxide, the positive active material which can constitute the cell excellent in the endurance in a charge-and-discharge cycle can be certainly manufactured by controlling the processing extent by making immersion time amount, the average size of microcrystal, or a lattice constant into an index. This positive active material is very useful as positive active material of a rechargeable lithium-ion battery etc. Moreover, since the nonaqueous electrolyte cell of this invention equipped with the positive electrode using this positive active material is excellent in the endurance over a charge-and-discharge cycle, it is useful as a rechargeable battery whose discharge property was stable.

---

[Translation done.]